Thermochimica Acta, 38 (1980) 285—291
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STUDIES ON DOUBLE SELENATES. I. THERMAL DECOMPOSITION OF LANTHANUM AND ALKALI METAL DOUBLE SELENATES

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(Received 2 November 1979)

ABSTRACT

Thermogravimetry, differential thermal analysis and other methods of analysis have been used to study the decomposition of hydrated lanthanum and alkali metal double selenates up to 1300°C. The results showed slight variations in the initial temperature of the various intermediate decomposition stages of the double selenates, as compared with the initial temperature of the corresponding decomposition of the simple selenates. The results also permitted the suggestion of mechanisms of thermal decomposition of these compounds.

INTRODUCTION

Several investigations have been carried out on the preparation and thermal behaviour of lithium [1], sodium [2—4], potassium [3,5,6], rubidium [6,7] and caesium [6,8] selenates [9], as well as lanthanum selenate [10,11]. The double selenates: $La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\,H_2O$ and $La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\,H_2O$, were described more than 100 years ago [12]. More recently, some other lanthanum and alkali metal double selenates have been reported [13,14]. No reference was found to the application of TG and DTA in the study of these double salts.

EXPERIMENTAL

Selenic acid and lanthanum selenate were prepared as described previously [10]. The alkali metal selenates were prepared by neutralization of a hot water solution of the corresponding alkali metal carbonates with a 25% water solution of selenic acid, as already described [9].

The double selenates were prepared by mixing 20 ml of 0.1 M solutions of

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the corresponding alkali metal and lanthanum selenates, and allowing the mixtures to evaporate in a desiccator over anhydrous calcium chloride at ambient temperature and pressure. The solutions were evaporated to near dryness and the formed crystals were removed from the mother liquor and kept in another desiccator over anhydrous calcium chloride until constant weight was reached.

Lanthanum ions were determined by the usual oxalate—oxide method and the alkali metal ions by atomic absorption spectroscopy in a Perkin—Elmer 403 atomic absorption spectrophotometer. Water of crystallization and selenium contents were determined through the TG curves.

The TG curves were obtained in a Deltatherm thermobalance D-4000-16, equipped with a Cahn Balance. A Pt/Pt—Rh 13% thermocouple was used as furnace temperature indicator. Samples of about 8 mg of material were placed in a 0.3 ml platinum crucible and heated at a rate of 5.2°C min^{-1} inside a ceramic hang-down tube in a static air atmosphere at ambient pressure.

The DTA curves were obtained in a four-channel Deltatherm D-2000-16 DTA module equipped with a Newport 260 digital thermometer and a furnace operating from ambient temperature up to 1600°C. Pt/Pt—Rh 13% differential thermocouples and a block temperature thermocouple were used. α-Alumina was used as the reference material. The samples were diluted to 20% in α-alumina and about 500 mg of these dilutions and reference material were tightly and homogeneously packed in the cylindrical holes of the inconel block of the specimen-holder assembly. The heating rate was 9.0°C min^{-1} under a static atmosphere at ambient pressure.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula, $La_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$ (Me = Li, Na, K, Rb, Cs).

The thermal decomposition of the lanthanum and alkali metal double selenates occurs in a characteristic way, depending on the alkali metal selenate present, as can be seen from the TG and DTA curves of Figs. 1 and 2, respectively.

All the reactions taking place during the thermal decomposition of the lanthanum and alkali metal double selenates can be summarized by the following equations.

$$La_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O \rightarrow La_2(SeO_4)_3 \cdot Me_2SeO_4 + n\ H_2O \qquad (1)$$

$$La_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow La_2(SeO_3)_3 \cdot Me_2SeO_3 + 2\ O_2 \qquad (2)$$

$$La_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow La_2(SeO_3)_3 \cdot Me_2SeO_4 + 1.5\ O_2 \qquad (3)$$

$$La_2(SeO_3)_3 \cdot Me_2SeO_3 \rightarrow La_2O_2SeO_3 \cdot Me_2SeO_3 + 2\ SeO_2 \qquad (4)$$

$$La_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow La_2O_2SeO_3 \cdot Me_2SeO_4 + 2\ SeO_4 + 1.5\ O_2 \qquad (5)$$

$$La_2O_2SeO_3 \cdot Me_2SeO_3 \rightarrow La_2O_3 \cdot Me_2SeO_3 + SeO_2 \qquad (6)$$

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Analytical results							
	Lanthanum (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8\ H_2O$	27.57	27.11	1.38	1.37	31.35	30.89	14.28	14.42
$La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\ H_2O$	28.19	27.94	4.66	4.68	32.04	31.56	9.13	9.19
$La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\ H_2O$	25.49	25.32	7.18	6.67	28.98	28.24	14.86	14.71
$La_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	23.85	23.25	14.68	14.96	27.12	26.84	12.36	12.56
$La_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	24.51	23.85	23.45	23.97	27.87	26.94	1.59	1.82

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the compounds: $La_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Temperature range of mass loss reactions in the TG curves (°C)							
	(1)	(2)	(4)	(5)	(6)	(7)	(8)	(9)
$La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8\ H_2O$	80–200	500–585	585–710		900–1045			1045–1160
$La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\ H_2O$	140–200			550–720		870–1040	1040–1250	
$La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\ H_2O$	80–160			580–700		900–1040	1040–1200	
$La_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	60–130			570–700		930–1025	1025–1130	
$La_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	100–170			590–750		900–1080		

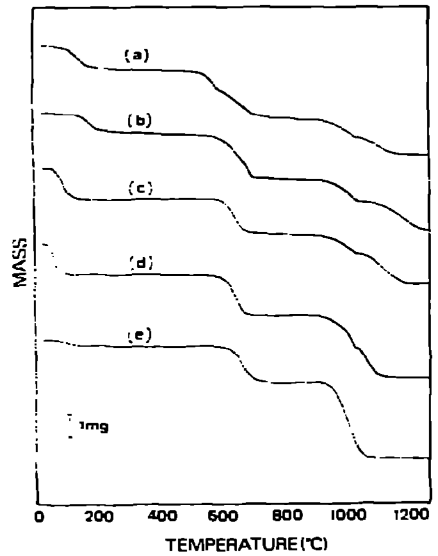

Fig. 1. TG curves of the double selenates of lanthanum and alkali metal. Heating rate: 5.2°C min^{-1}. (a) $La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8\,H_2O$ (7.38 mg); (b) $La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\,H_2O$ (7.62 mg); (c) $La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\,H_2O$ (7.48 mg); (d) $La_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\,H_2O$ (8.76 mg); and (e) $La_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$ (8.26 mg).

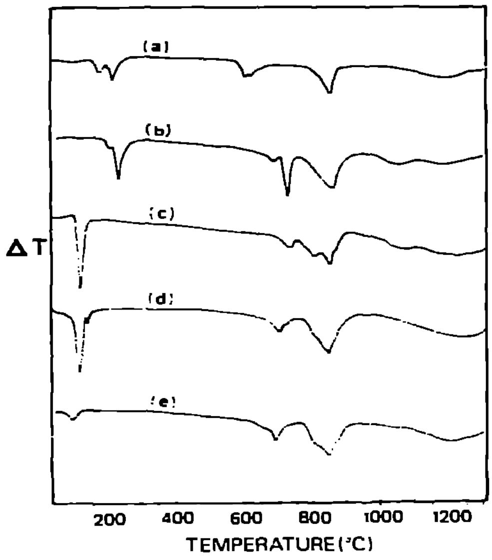

Fig. 2. DTA curves of double selenates of lanthanum and alkali metal, diluted to 20% in α-alumina. Heating rate: 9.0°C min^{-1}. (a) $La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8\,H_2O$; (b) $La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\,H_2O$; (c) $La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\,H_2O$; (d) $La_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\,H_2O$; and (e) $La_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$.

$$La_2O_2SeO_3 \cdot Me_2SeO_4 \rightarrow La_2O_3 + Me_2SeO_4 + SeO_2 \qquad (7)$$

$$La_2O_3 \cdot Me_2SeO_4 \rightarrow La_2O_3 + |Me_2SeO_4| \qquad (8)$$

$$La_2O_3 \cdot Me_2SeO_3 \rightarrow La_2O_3 \cdot Me_2O + SeO_2 \qquad (9)$$

Table 2 attributes to each compound the probable set of the above reactions and their temperature ranges in correspondence with the various mass losses observed in the TG curves.

Table 3 gives the temperature of the DTA peaks (all endothermic) in correspondence with the reactions or fusion occurring for each compound.

With respect to the TG curves, the change of slope due to the formation of lanthanum selenite [11] is evident only in lanthanum and lithium double selenate at 585°C; in lanthanum and sodium double selenate it is barely visible at 615°C; in the TG curve of the other double selenates this change of slope is not visible, probably because of the almost simultaneous formation of lanthanum selenite and (di)oxyselenite. All double selenates gave positive tests for selenite ion in the presence of selenate ion [15] after being heated at 650°C. In the case of lanthanum and lithium double selenate, the formation of lanthanum (di)oxyselenite occurs with partial reduction of lithium selenate to lithium selenite [9].

Above 900°C the lanthanum (di)oxyselenite formed in the previous step undergoes decomposition to La_2O_3 and SeO_2. In the case of lanthanum and

TABLE 3

Temperature of DTA peaks (all endothermic) in correspondence with reactions and fusion of the compounds: $La_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Peak temperature in DTA curves (°C)									
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Fusion
$La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8\ H_2O$	177–220	630		865		1200			1200	610
$La_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\ H_2O$	220–240		690		860		1050	1250		740
$La_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 9\ H_2O$	117		740		810		1080	1250		860
$La_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	100–147		750		810			1200		850
$La_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	95–215		690		810			1200		850

sodium double selenates this decomposition probably occurs with partial reduction of sodium selenate to sodium selenite [9].

The last step of the TG curves of the lanthanum and alkali metal double selenates depends upon the nature of the alkali metal considered [9]. Above 1040° C the lithium selenite partly decomposes to lithium oxide and the remainder evaporates so that the residue at 1160° C contains La_2O_3 and about 70% of the theoretical amount of LiO_2. The same probably occurs with the mixture of sodium selenite and selenate that also undergoes decomposition and evaporation but, as the second process predominates, the residue at 1245° C contains La_2O_3 and only about 30% of the theoretical amount of Na_2O.

The final mass loss of the other double selenates (La—K, La—Rb and La—Cs) is due to evaporation of the corresponding alkali metal selenate and seems to occur without intermediate formation of alkali metal selenite. It has already been observed that when potassium selenite is heated in an atmosphere of air above 900° C it is quantitatively oxidized to potassium selenate [5].

In the case of lanthanum and caesium double selenates the final mass loss corresponds to simultaneous decomposition of the lanthanum (di)oxyselenite to La_2O_3 and SeO_2 and total evaporation of caesium selenate, so that the final residue at 1070° C contains only La_2O_3. The final residue of lanthanum and potassium (at 1185° C) and lanthanum and rubidium (at 1115° C) similarly contains practically only La_2O_3.

The DTA curves of Fig. 2 show peaks in correspondence with all mass losses visible, or in some cases not visible, in the TG curves, and peaks in correspondence with fusion. The temperature of each DTA peak and its probable interpretation are summarized in Table 3.

CONCLUDING REMARKS

The thermal behaviour of the lanthanum and alkali metal double selenates revealed some variations as compared with the thermal behaviour of the corresponding simple selenates so that each double selenate presents typical TG and DTA patterns.

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